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POLYPHOSPHAZENES

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POLYPHOSPHAZENES

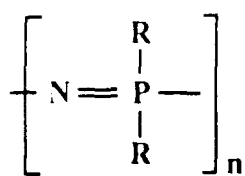
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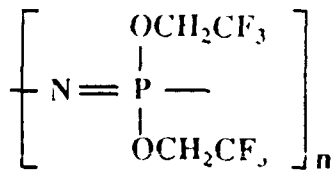
BACKGROUND

The field of inorganic-organic macromolecules provides a common connecting point to the well-established areas of ceramics, metals, semiconductors, and classical organic polymers (Figure 1). In no system is this relationship clearer than in the field of polyphosphazenes, where controlled changes in macromolecular structure allow the formation of materials that are polymer-like, ceramics-like, or metal- or semiconductor-like.

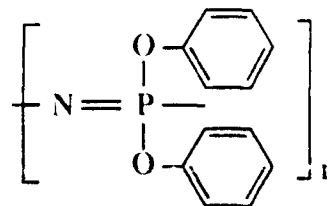
Polyphosphazenes are long-chain macromolecules that contain a backbone of alternating phosphorus and nitrogen atoms, with two organic, inorganic, or organometallic side groups attached to each phosphorus, as shown in structure 1. Because of the unusual methods of synthesis (see later) an almost infinite variety of side groups and combinations of different side groups can be linked to the backbone. Examples of several well-studied poly(organophosphazenes) are shown in structures 2-5.¹⁻⁵



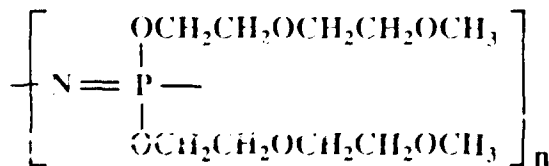
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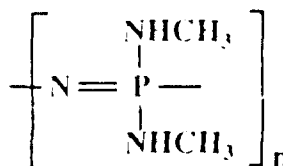
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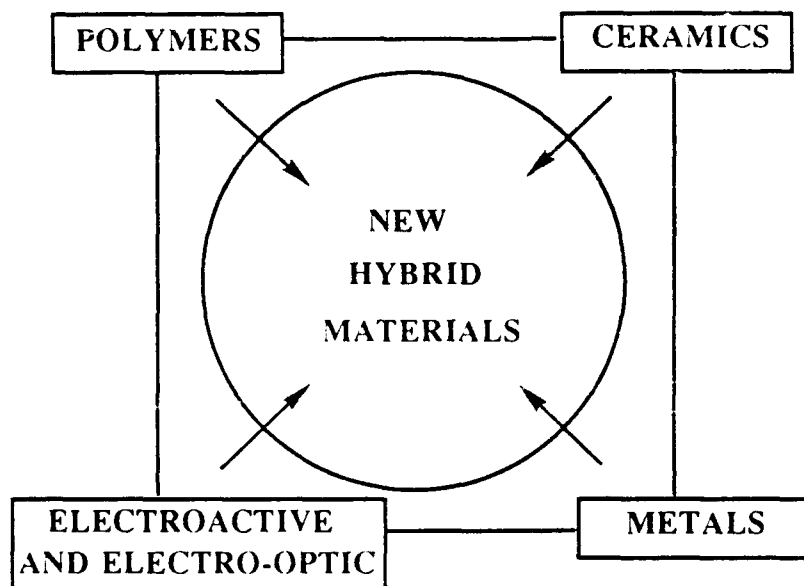


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TYPES OF MATERIALS

Easily fabricated, strong, flexible,
corrosion resistant, electrical
insulating, and inexpensive.
But thermo-oxidatively sensitive

Inert, rigid, thermally stable,
and often inexpensive.
But heavy and brittle



Vital for communications.
But difficult to fabricate,
and expensive

Strong, usually inexpensive, and
good electrical conductors.
But heavy and prone to corrosion

Figure 1. The four classical types of materials and their relationship to new hybrid materials that combine the strengths and minimize the weaknesses of existing substances.

Different side groups generate different molecular and materials' properties. For example, polymers **2** and **3** are hydrophobic, film- and fiber-forming materials. By contrast, polymer **4** is a water-soluble elastomer, and polymer **5** is a water-soluble amorphous glass. Thus the key feature of polyphosphazene chemistry is the concept of molecular design by the linkage of different side groups to the inorganic skeleton, and the translation of this molecular tailoring into materials with new combinations of properties.

By the end of 1990 roughly 300 different types of polyphosphazenes had been synthesized and characterized, approximately 2000 publications and patents had appeared, and new publications and disclosures were appearing at a rate of about 170-200 each year. Thus, this is a broad and rapidly expanding field with many opportunities for fundamental chemical synthesis and structure-property studies, and many possibilities for technological developments.

This overview of polyphosphazene chemistry and technology is deliberately brief because comprehensive surveys of the field have been published recently or are in press.⁶⁻¹⁴ Moreover, the elementary small-molecule background has been covered in a book¹⁵ and in recent survey articles.¹⁶⁻¹⁷ Additional aspects of this subject that deal with new synthesis pathways and materials properties have been reviewed elsewhere.¹⁸⁻²⁰ Thus, the focus of this report is on the underlying concepts, and on recent work from our laboratory.

SYNTHESIS OF POLYPHOSPHAZENES

There are three main approaches to polyphosphazene synthesis -- the ring-opening polymerization followed by macromolecular substitution route, the cyclic trimer substitution followed by ring-opening polymerization route, and the condensation method. The first two methods have been the main focus of our

program.^{1-5, 21-34} The last approach was developed in other laboratories and is described elsewhere.^{18,19,35,36}

Ring-Opening Polymerization Followed By Macromolecular Substitution.

This approach has provided access to by far the largest variety of polyphosphazene molecules. The process begins with the manufacture of the small molecule starting material, hexachlorocyclotriphosphazene (**6**), from phosphorus pentachloride and ammonium chloride using a reaction first reported by Liebig in 1834³⁷ and modified by Schenk and Romer in 1924.³⁸ The following steps were discovered and developed in our program¹⁻⁵ and are summarized in Scheme I.

Scheme I near here

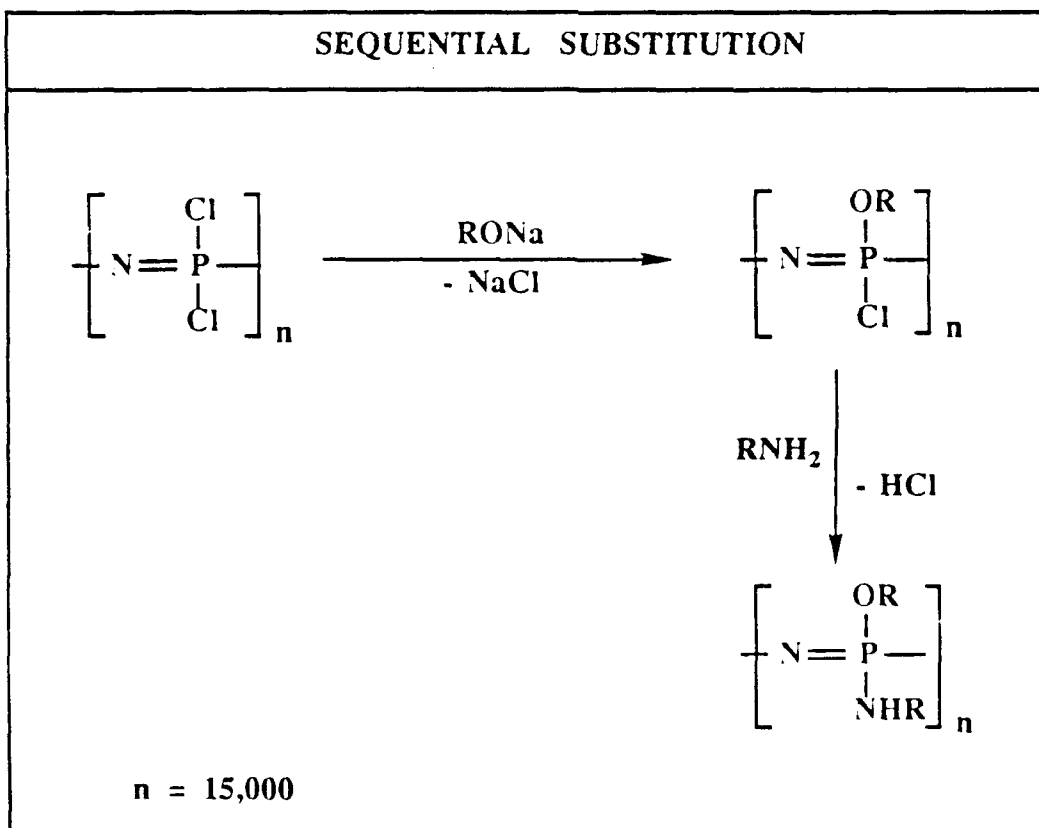
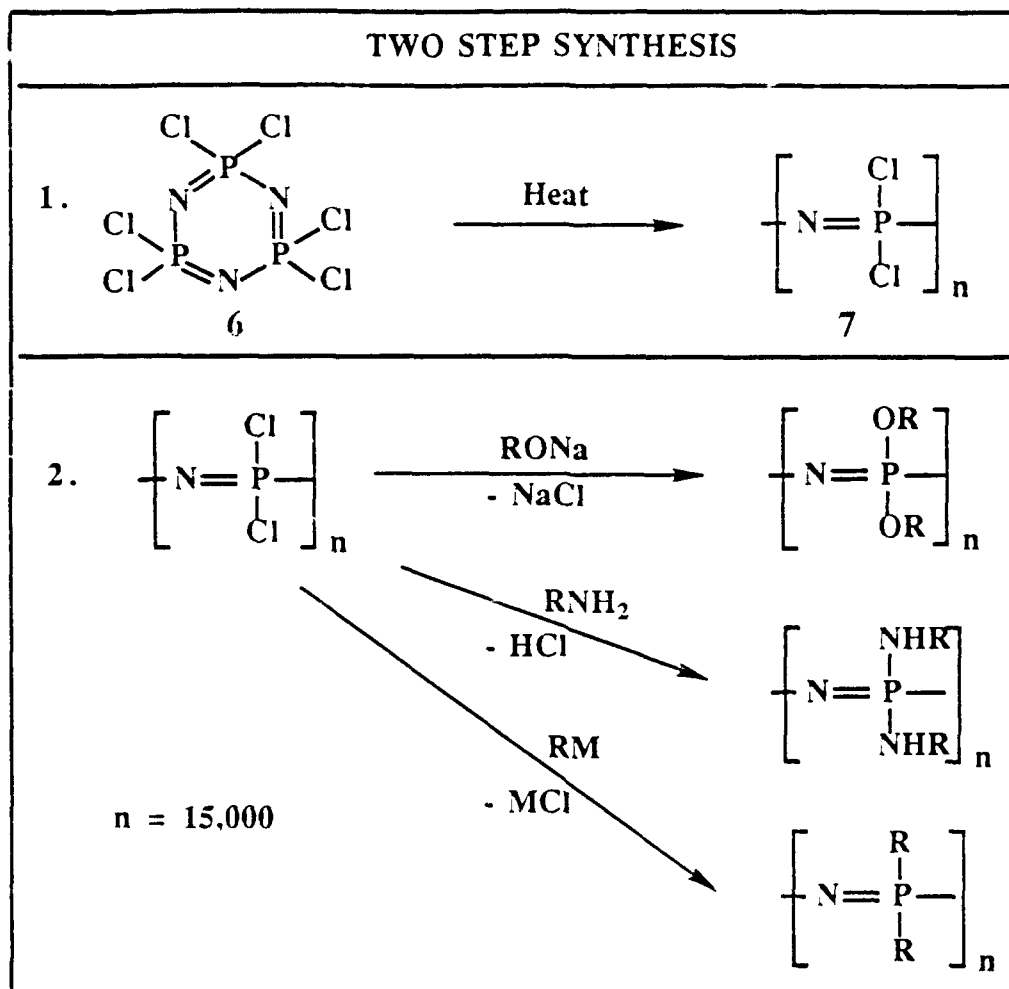
Careful heating of cyclic trimer **6** brings about its ring-opening polymerization to an uncrosslinked, organic-soluble high polymer known as poly(dichlorophosphazene) (**7**). This polymer, which typically contains an average of 15,000 repeating units per chain, is a remarkable macromolecular intermediate. The high reactivity of the phosphorus-chlorine bonds allows access to nucleophilic substitution reactions in which the chlorine atoms are replaced by a wide variety of organic, organometallic, or inorganic side groups. The availability of a broad range of nucleophilic reagents allows access to hundreds of different polymer structures. Moreover, two or more different types of side groups can be introduced by simultaneous or sequential reactions, as shown in Scheme II.

Scheme II near here

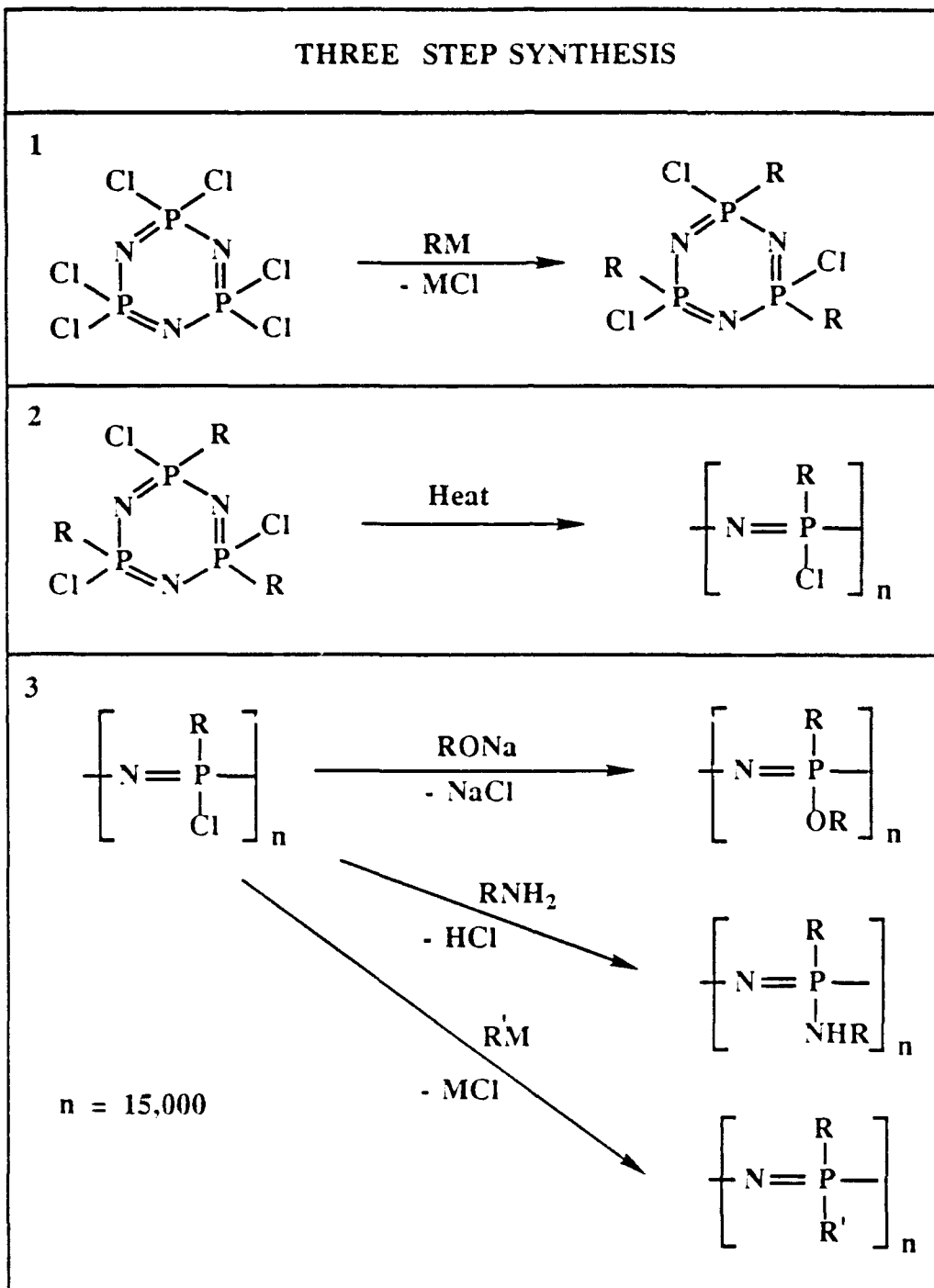
Cyclic Trimer Substitution Followed By Ring-Opening Polymerization.

This is illustrated in Scheme III.²⁸⁻³⁴

Scheme III near here



Scheme III



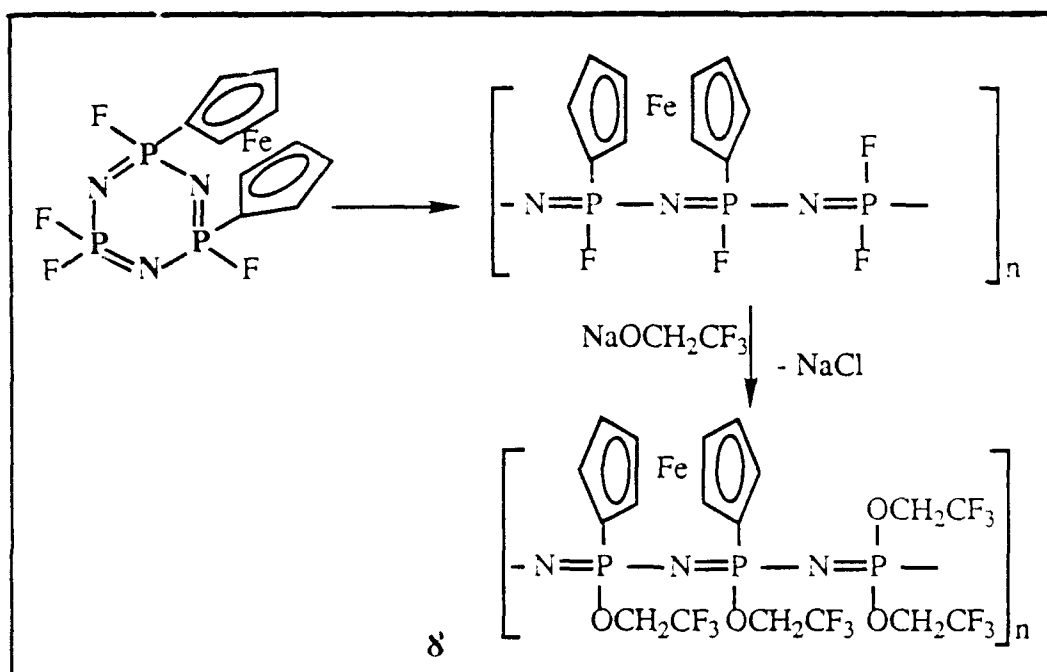
Certain synthetic advantages exist if the chlorine substitution reactions are carried out at the cyclic trimer level rather than at the stage of the high polymer. For one thing, the substitution reactions may be faster, and purification processes may be easier. However, extensive work in our laboratory has shown that, in general, the higher the loading of organic groups on the cyclic trimer, the lower is the tendency for the small-molecule species to polymerize. Ring-expansion reactions may occur readily, but high polymer formation may be difficult. Two solutions to this problem have been devised. First, a compromise can be made in which several chlorine atoms are left attached to the trimer. This allows polymerization to occur, but it requires a final macromolecular substitution step to remove the chlorine atoms and ensure hydrolytic stability. Second, fully organo-substituted cyclic trimers will polymerize if ring strain is generated either by the introduction of trans-annular bridging groups, such as ferrocenyl units (Scheme IV), or by the presence of additional heteroelements, such as carbon or sulfur, in the ring (see later).

Scheme IV near here

MOLECULAR DESIGN AND TAILORED PROPERTIES

Certain properties in polyphosphazenes can be attributed to the inorganic backbone, and other properties are due to the presence of specific side groups. The phosphorus-nitrogen backbone is responsible for the underlying high skeletal flexibility, the thermo-oxidative and photo-oxidative stability, and the broad electromagnetic transmission window which extends from the near infrared to the short wave ultraviolet.

On the other hand, the polyphosphazene chain also serves as a carrier or "platform" for the specific side groups, with each side group imposing its own special properties on to the system. For example, the side groups play a



dominant role in determining the overall flexibility of each polymer molecule (which is the sum of contributions from the inherent flexibility of the skeleton plus the polar and steric restrictions imposed by the side groups). Bulky and rigid side groups raise the glass transition temperature, whereas flexible side groups allow the torsional freedom of the backbone bonds to become manifest in glass transitions as low as -100°C . Specific side groups provide biological or biomedical attributes, while others generate high refractive index, non-linear optical, photochromic, electroactive, or ceramic-generating behavior. It is this ability to fine tune the properties through the choice of side groups that underlies the applications for polyphosphazenes.

APPLICATIONS

The relationship between polymer structure, properties, and applications for polyphosphazenes is a very broad subject, and only three sets of examples will be mentioned here. These areas are summarized in Figure 2.

Figure 2 near here

Phosphazene High Performance Elastomers. Elastomers are materials that contain highly flexible polymer molecules. They have glass transition temperatures below room temperature and, in most cases, the materials structure is not stiffened by the presence of microcrystallites. In polyphosphazene science this translates into a need for flexible side groups, plus a lack of molecular symmetry in order to prevent the close packing of chains that normally gives rise to crystallization. Four main classes of polyphosphazenes have useful elastomeric properties. These are illustrated by structures 9-11 and 4.

The so-called phosphazene fluoroelastomers (9) were first described by Rose³⁹ as an outgrowth of our earliest studies.¹⁻³ The first stable polyphosphazenes contained only one type of side group per molecule, as in

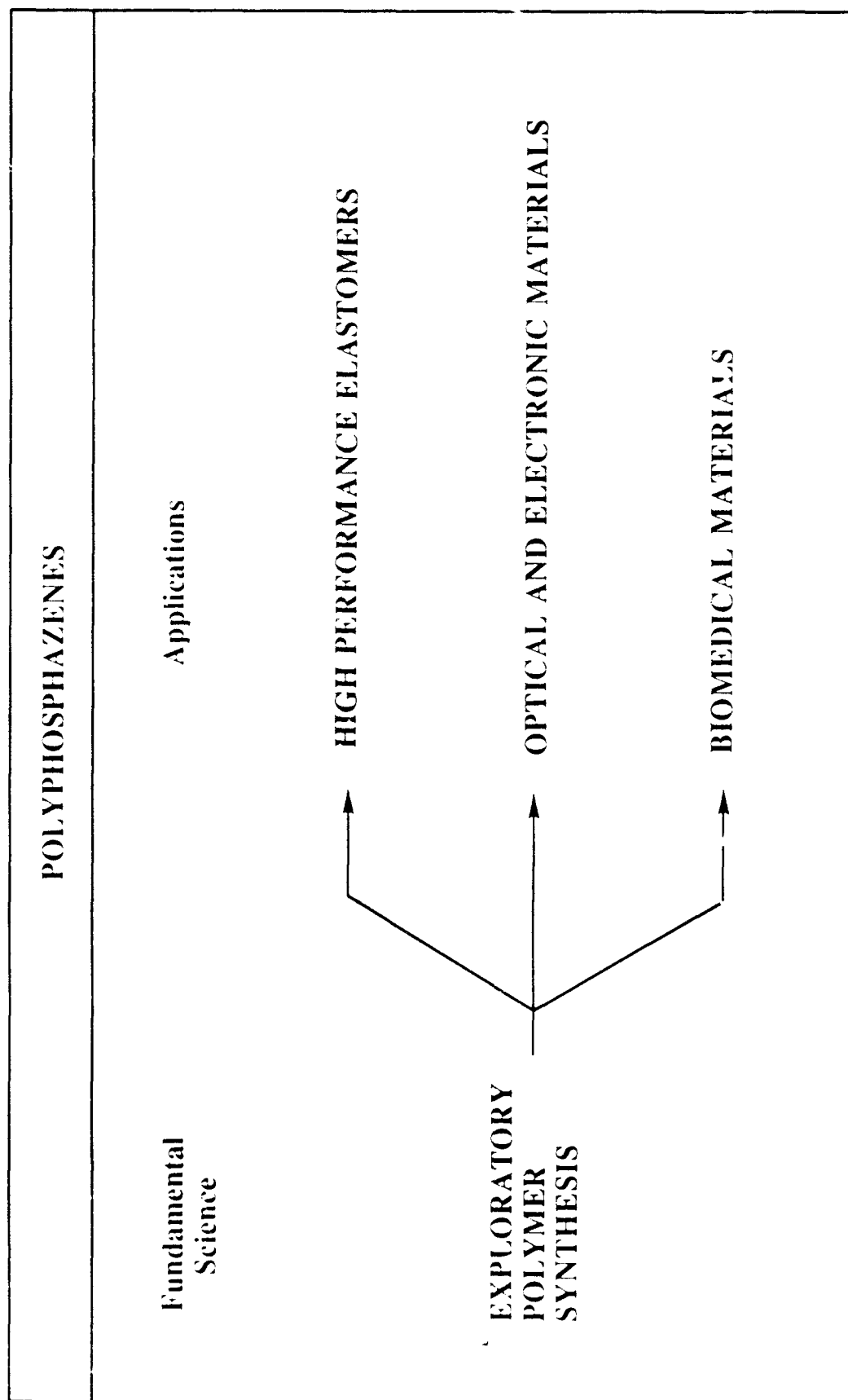
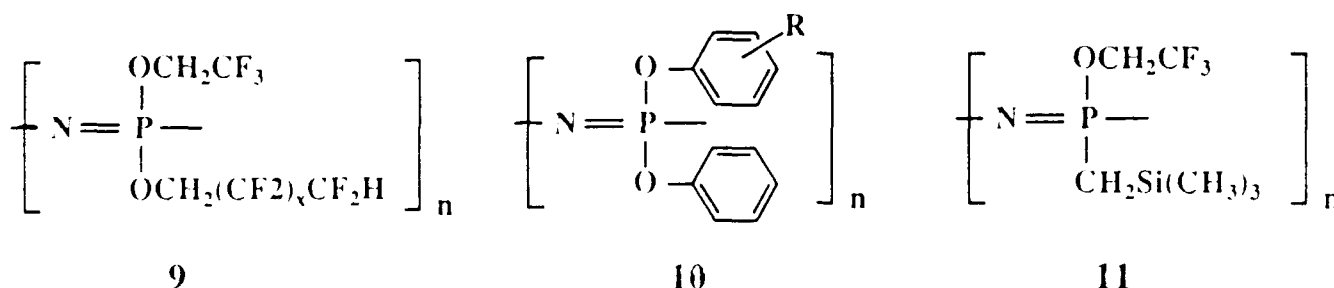


Figure 2

polymers **2** and **3**. If only one type of fluoroalkoxy side group is present, as in structure **2**, the polymer is a non-burning, hydrophobic, microcrystalline, film- and fiber-forming material. But if two or more fluoroalkoxy side groups are present along the same polymer chain, the material becomes a low-glass-transition, hydrophobic, solvent-, oil-, and hydraulic fluid-resistant elastomer that is the basis of numerous engineering developments.^{13,14,40} Similarly, mixed-substituent aryloxy-derivatives, such as **10**, are used commercially as non-burning, low smoke forming elastomers for thermal and electrical insulation.¹³



The introduction of organosilicon side groups, as in **11**,⁴¹⁻⁴⁴, creates a series of elastomers that are hybrids of polyphosphazenes and poly(organosiloxanes). These, too, appear to have a promising future in advanced engineering and in medical technology.

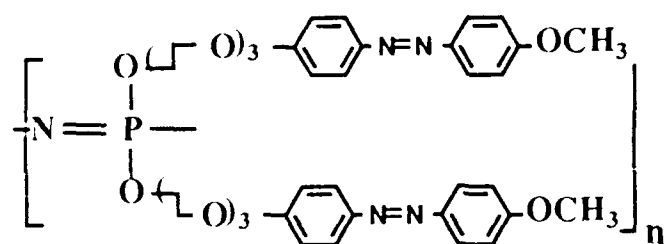
Finally, one of the most intriguing elastomers is the one shown as structure **4**,^{5,45-49} This polymer, known as MEEP, is an excellent solid solvent for salts such as lithium triflate. The polymer-salt conjugate conducts electricity by an ionic mechanism, and has a room-temperature conductivity several orders of magnitude better than polyethylene oxide systems, which have been the standard for research and development work in the past. The MEEP-lithium triflate system, lightly crosslinked to generate dimensional stability, is a leading candidate for use as the solid electrolyte in lightweight, rechargeable lithium batteries.

Electro-Optical Materials. The polyphosphazene skeleton is an excellent "platform" for organic or organometallic side groups that confer special electronic or optical properties on the polymeric material. Many examples of this principle have been studied in our program. Here, we will discuss three cases that illustrate the possibilities.

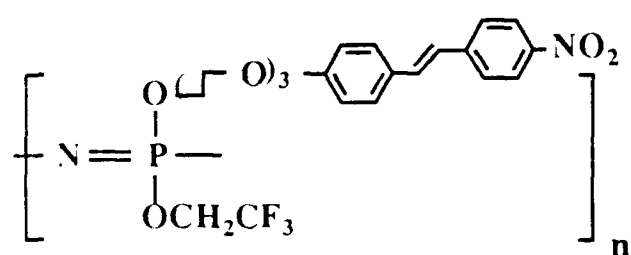
First, the introduction of ferrocenyl side groups, as in polymer **8**, provides sites for electrochemical oxidation and reduction.⁵⁰⁻⁵⁴ The actual electrochemical behavior can be tuned by the choice of cosubstituent side groups, and by the mode of linkage of the metallocene to the polymer chain (one link or two). These polymers serve as electrode mediator materials in electron transfer processes, and have possible uses in electrochemical catalysis, battery technology, and new semiconductor devices.

Polymer **12** shows liquid crystalline behavior as a consequence of the ability of the side group mesogens to become aligned in the quasi-liquid state, a process that is facilitated by the high torsional flexibility of the backbone and the spacer groups.⁵⁵ This is a general phenomenon that exists when a variety of organic side group structures are present.^{56,57}

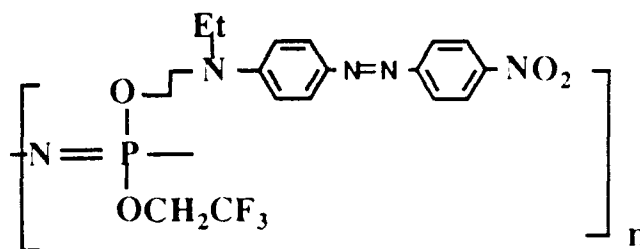
Finally, polymers of type **13** and **14** can be poled by application of an electric field to align the polarizable aromatic side groups and generate second order non-linear-optical properties.^{58,59} Polymer **14** has one of the highest second harmonic coefficients known for a macromolecular material (34-46 pm/V), even though the effect is lost after removal of the poling field due to thermal randomization of the side groups.



12

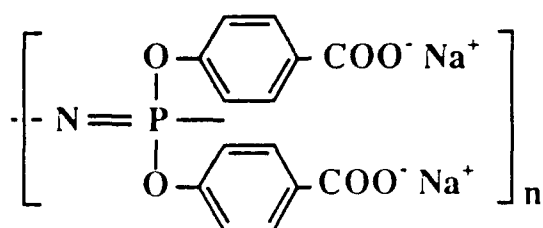


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14

Biomedical Polyphosphazenes. Biomedical applications exist for a wide range of polyphosphazenes, from inert biomaterials for cardiovascular and dental uses, to bioerodable and water-soluble polymers for controlled drug delivery applications.⁶⁰ Here we will focus on a recent discovery that promises to have widespread use in the fields of the artificial liver, pancreas, and endocrine glands, and in the production of protein antibodies and antigens.⁶¹⁻⁶² The system is illustrated in Structure 15 and in Figure 3.



15

Polyphosphazene 15 is soluble in water as its sodium salt.⁶³ However, when aqueous solutions of the polymer are brought into contact with solutions of di- or tri-valent cations, the chains are crosslinked via the ionic units. This converts the water-soluble polymer to a hydrogel. This is the basis of a method for the microencapsulation of living cells, such as liver cells, or of protein-producing cells.^{61,62} As shown in the figure, each cell or cluster of cells becomes coated with a hydrogel membrane that allows nutrients and cell metabolic products to enter and escape, but shields the cells from the antibodies of the host. Thus, long-lived liver- or pancreatic-support devices are accessible via this technology. Other polyphosphazenes have been used as insoluble support surfaces for the immobilization of enzymes and catecholamines, and these too are promising systems for use in biomedical technology.^{64,65}

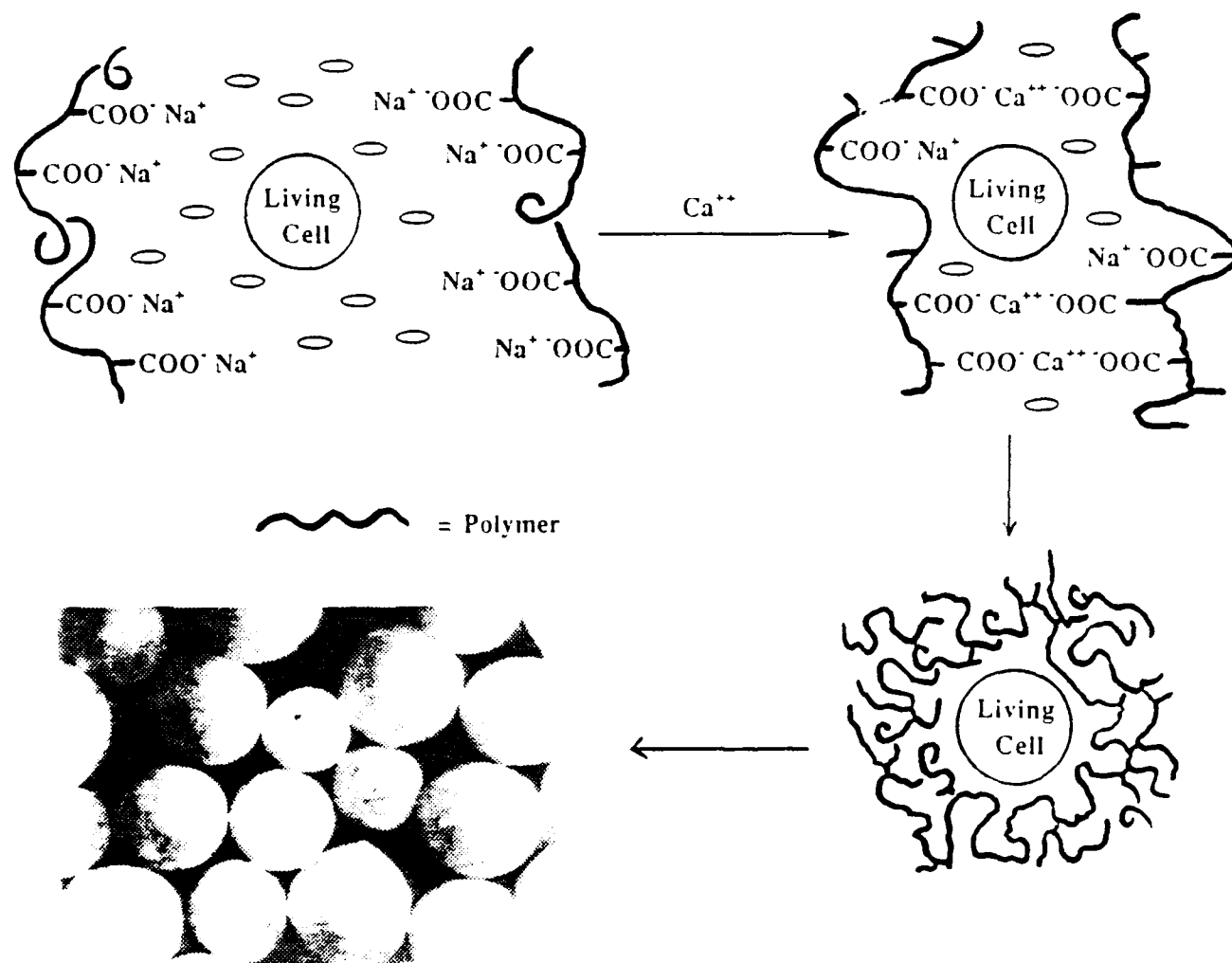


Figure 3 Ionic crosslinking of polymer 15 to form hydrogel microspheres.

CONCLUSIONS

In the realm of polymer chemistry, polyphosphazenes occupy a virtually unique position at the point of connection between petrochemical-, mineralogical-, and biological polymers, as shown in Figure 4.

Figure 4 near here

Perhaps their most important feature is the ease with which changes in side groups allow the properties to be biased in the direction of classical organic polymers, inorganic materials, or biological macromolecules, providing combinations of properties not found in the classical areas. They can be viewed as universal polymers with uses that extend throughout the fields of structural and elastomeric materials, engineering, and medicine. In this sense, they are the prototype inorganic-organic polymers of the future that point the way to the evolution of other systems that contain heteroelements other than phosphorus and nitrogen. A step in this direction has already taken place with the discovery of synthesis methods that yield poly(carbophosphazenes)⁶⁶ and poly(thiophosphazenes)⁶⁷ (Schemes V and VI), and these are undoubtedly forerunners of other new polymer systems with unique properties and advanced uses.

Schemes V and VI near here

ACKNOWLEDGMENTS

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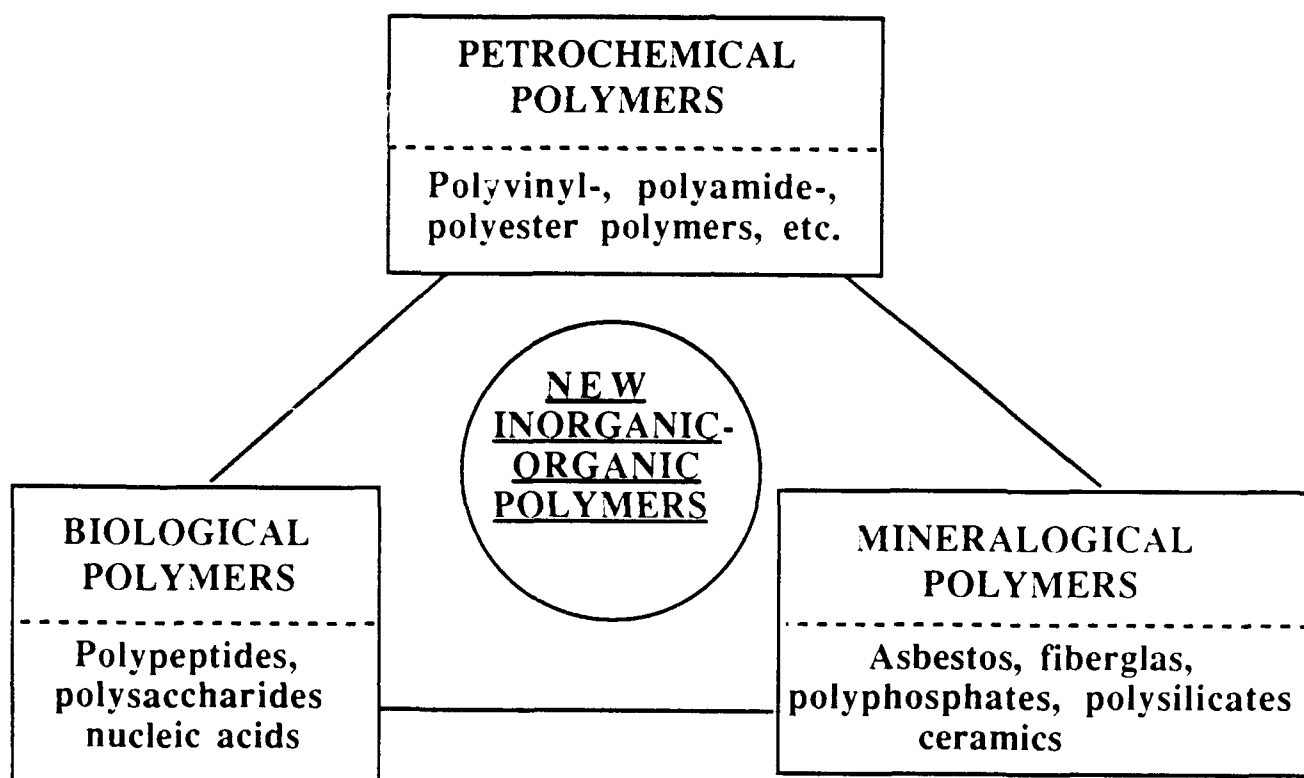
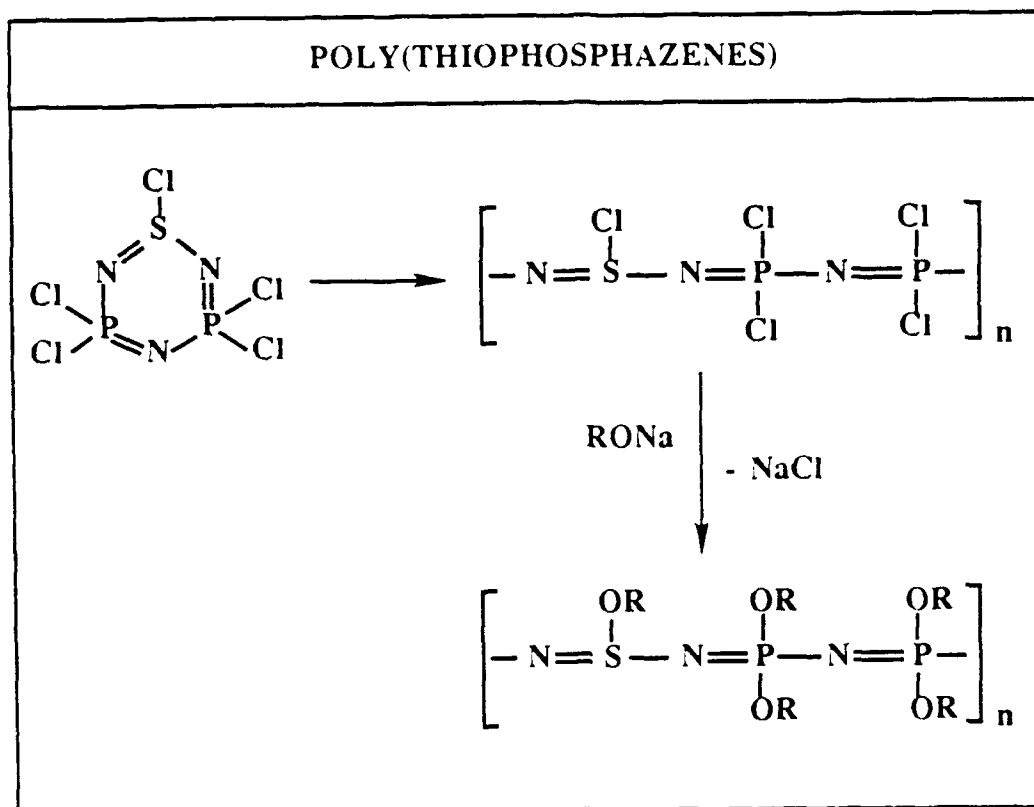
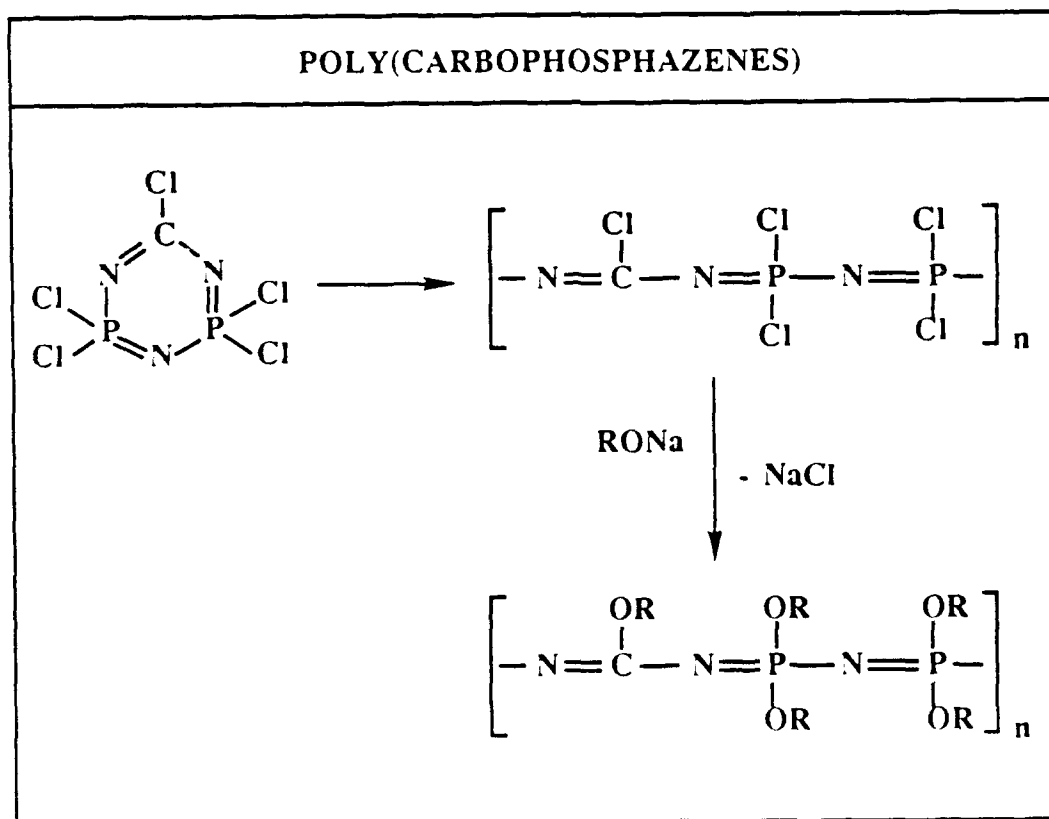


Figure 4. The three types of classical polymers, and the central position of inorganic-organic polymers in future developments.



Scheme V



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